

Unsaturated Alcohol Esters of the 9,10-Dihydroxystearic Acids. Preparation of Elaidyl Alcohol

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During a recent investigation it was necessary to identify a series of by-products which appeared to be unsaturated alcohol esters of 9,10-dihydroxystearic acid. A search of the literature revealed that none of these compounds had been described previously. To facilitate their identification, we have prepared the allyl, methallyl, β -chloroallyl, furfuryl, cinnamyl, oleyl and elaidyl esters of both 9,10-dihydroxystearic acids, m. p. 95 and 130°, respectively.

Elaidyl alcohol is not a very well-known compound, since its preparation is extremely tedious. It is usually prepared by reduction of purified methyl or ethyl elaidate with metallic sodium and absolute alcohol, and purified by fractional distillation and crystallization.² We have worked out a convenient method for its preparation in fair yield from commercial or highly purified oleyl alcohol. Elaidyl alcohol, m. p. 36–37°, is obtained as glistening plates.

Experimental

Materials.—Low melting 9,10-dihydroxystearic acid (m. p. 95°) and its high-melting isomer (m. p. 130°), and their methyl esters (m. p. 70 and 104°, respectively) were prepared as previously described.^{3,4} Purified oleyl alcohol was prepared from the commercial grade by low temperature solvent crystallization and fractional distillation.⁵ The allyl, methallyl, β -chloroallyl, cinnamyl and furfuryl alcohols were the purest commercial grades and were fractionally distilled before use.

(1) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Not copyrighted.

(2) Toyama, *Chem. Umschau Fette, Öle, Wachse Harze*, **31**, 13 (1924).

(3) Swern and Jordan, *THIS JOURNAL*, **67**, 902 (1945).

(4) Swern, Billen, Findley and Scanlan, *ibid.*, **67**, 1786 (1945).

(5) Swern, Knight and Findley, *Oil & Soap*, **21**, 133 (1944).

Two alternative procedures were employed for the preparation of elaidyl alcohol.

1. Commercial oleyl alcohol (oleyl alcohol content, 60 to 70%) was distilled through an 18-inch Vigreux column, and the fraction boiling at 165–205° (4.3 mm.), which amounted to about 85% of the starting material, was retained. Six hundred grams was dissolved in 9000 ml. of acetone, and the solution was cooled to –20° to precipitate solid (saturated) alcohols. The liquid alcohols (470 g.), obtained from the filtrate, were heated and stirred for two hours in a nitrogen atmosphere at 220–225° with 0.3% of powdered selenium.⁶ The cooled reaction mixture was dissolved in 4700 ml. of acetone, treated with active carbon and filtered, and the filtrate was cooled to –20°. The precipitate, m. p. about 30°, consisted mainly of elaidyl alcohol and weighed 200 g. Pure elaidyl alcohol, m. p., 36–37° (lit. 35–35.5°),² was obtained after one additional crystallization from acetone at –20° and two at 0°. The yield was 56 g. *Anal.* Iodine number: Calcd., 94.5; Found, 93.4.

2. Purified oleyl alcohol⁵ (270 g., oleyl alcohol content, 97%) was isomerized as described above. Crystallization from acetone at –20°, after treatment of the solution with active carbon, yielded 164 g. of fairly pure elaidyl alcohol m. p. about 33°; iodine number, about 91. Pure elaidyl alcohol, m. p., 36–37°, was obtained after one additional crystallizations from acetone at 0 to –5°. The yield was 110 g. Iodine number was 93.6.

Esterification Procedures.—The allyl, β -chloroallyl, oleyl and elaidyl esters were prepared by direct esterification of the corresponding alcohol with the dihydroxystearic acids, previously reported methods being employed.³ In these preparations, with the exception of the allyl esters, the azeotropic method was used. Approximately 2–3 ml. of allyl and β -chloroallyl alcohol per gram of acid were employed, as compared with 20% molar excesses of oleyl and elaidyl alcohols. Yields of crude esters were quantitative.

The methallyl, furfuryl and cinnamyl esters were prepared by alcoholysis of methyl 9,10-dihydroxystearate with the appropriate alcohol. A typical preparation is as follows: To 0.5–1.0 mole of the freshly distilled alcohol, 0.4 g. (0.017 mole) of metallic sodium was added slowly at room temperature. When the sodium was completely dissolved, 0.05 mole of methyl 9,10-dihydroxystearate was added, and the mixture was heated on the steam-bath for three hours in a nitrogen atmosphere, with occasional shaking. The methyl alcohol formed in the reaction was permitted to escape. The reaction mixture was poured into a large quantity of hot water, and the aqueous layer was separated and discarded. The product was washed with hot water and cooled to room temperature. The solid product obtained was crystallized to constant melting point from 95% ethyl alcohol (2 to 5 ml./g.).

(6) Bertram, *Chem. Weekblad*, **33**, 3 (1936).

TABLE I
UNSATURATED ALCOHOL ESTERS OF 9,10-DIHYDROXYSTEARIC ACID

Ester	Melting point, 95°						Melting point, 130°					
	Yield, ^a %	M. p., °C.	Sapn. no.		Iodine no.		Yield, ^a %	M. p., °C.	Sapn. no.		Iodine no.	
			Calcd.	Found	Calcd.	Found			Calcd.	Found	Calcd.	Found
Allyl	30	59.8-60.7	157.4	158.1	71.2	70.0	46	98.8-99.1	157.4	157.1	71.2	71.4
Methallyl	58	60.5-61.0	151.4	151.9	68.4	68.4	53	92.8-93.3	151.4	151.4	68.4	67.6
β-Chloroallyl ^b	52	67.3-67.7	59	98.2-98.4 ^c
Furfuryl	36	69.9-70.2	141.5	143.0	51	99.0-99.3	141.5	142.5
Oleyl	50	52.0-52.4	98.9	101.3	44.8	43.6	67	79.9-80.2	98.9	100.2	44.8	43.8
Elaidyl	53	70.2-70.7	98.9	101.3	44.8	43.9	70	84.7-85.2	98.9	101.0	44.8	44.6
Cinnamyl	42	74.4-74.9	129.7	130.1	34	101.1-101.4	129.7	131.5

^a Purified products, after at least three crystallizations from 95% ethanol. ^b (Low melting point) Calcd.: C, 64.6; H, 10.1. Found: C, 64.8; H, 9.8. (High melting point) Calcd.: C, 64.6; H, 10.1. Found: C, 64.8; H, 9.9. ^c The theoretical iodine number could not be obtained (*cf.* Shriner, "Quantitative Analysis of Organic Compounds, 2nd ed., 1941, p. 51).

Results and Discussion

The results are summarized in Table I. With the exception of the furfuryl ester, which becomes slightly yellow after exposure to light and air, the products are white, crystalline solids. The esters prepared from the low-melting form of 9,10-dihydroxystearic acid are insoluble in water and Skellysolve B, and soluble in 95% ethanol, acetone, toluene, ethyl acetate and nitropropane. The esters prepared from the high-melting form

of 9,10-dihydroxystearic acid are also insoluble in water and Skellysolve B, but only slightly soluble at room temperature in the other solvents mentioned. On gentle warming, however, they dissolve readily. Preliminary investigation indicated that some of these compounds may be good plasticizers for ethyl cellulose and cellulose acetate.

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